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ELECTRONIC PROPERTIES OF FULLERENES

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Abstract Systematic investigation of the electronic properties of fullerenes C_N ($N = 60, 70, 76, 78, 82, 84, 86$) has been made by cyclic voltammetry, optical absorption, and photo-ionization measurements. The HOMO-LUMO gap decreases monotonically with increase of number of carbon atoms (N) and shows a characteristic 1/ N-dependence comparing with those of polyenes and aromatic hydrocarbons. As a reflection of large molecular size, the Coulomb-repulsive energy ,U', is considerably small less than 0.4 eV and decreases further with increase of molecular size.

Keywords: Higher fullerene, Electronic property, Cyclic voltammetry

INTRODUCTION

The production[1] of C_{60} and higher fullerenes C_N offers a unique opportunity to study the effects of size and geometry of molecules in the π-conjugate systems. In the normal polyene, the HOMO-LUMO gap decreases monotonically with increase of the chain length due to delocalization of π-electron along the chain but a finite gap still remains for an infinite chain due to the Peierls instability. While, graphite, which has the 2-D plane structure, is a zero-gap semiconductor. A series of fullerenes has a cage structure in a nano-scale, and they can be regarded as an intermediate π-conjugate system between the polyene system and graphite. Although a change of number of carbon atoms in higher fullerenes is accompanying with a geometric change of cage, the ionization energy seems to decrease in higher fullerenes, which is qualitatively consistent with the prediction from the MO calculations.[2] While, individual characters of higher fullerenes definitely appear in several experiments such as in preparation of metallofullerenes,[3] crystallization, and alkaline-metal doping.[4] Thus, a general consideration of higher fullerenes is not straightforward, and the essential features of higher fullerenes have been scarcely discussed due to the complexity of their structures.

In this report, focusing on the number of carbon atoms (N), we examine the HOMO-LUMO gap, the coulomb repulsive energy in a molecule, and the ionization potential by using cyclic voltammetry (CV), optical absorption, and photo-ionization measurements on fullerenes C_N (N = 60, 70, 76, 78, 82, 84, 86), except for the photo-ionization measurement on C_{86}. The consistency of the CV and the optical data allows us to discuss the effective electron-electron repulsive energies in details. In addition, a comparison of the 1/N-dependence of the optical gap with those of polyene, aromatic hydrocarbon and graphite provides useful information to understand an essential feature of the cage structure of fullerenes.

EXPERIMENTS

Fullerenes C_N (N=60, 70, 76, 78, 82, 84, 86) were extracted from soot with a high-performance liquid chromatography (Buckyclucher I column), using the toluene and hexane (1:1) mixed solvent. From the analysis of the laser-desorption time-of-flight

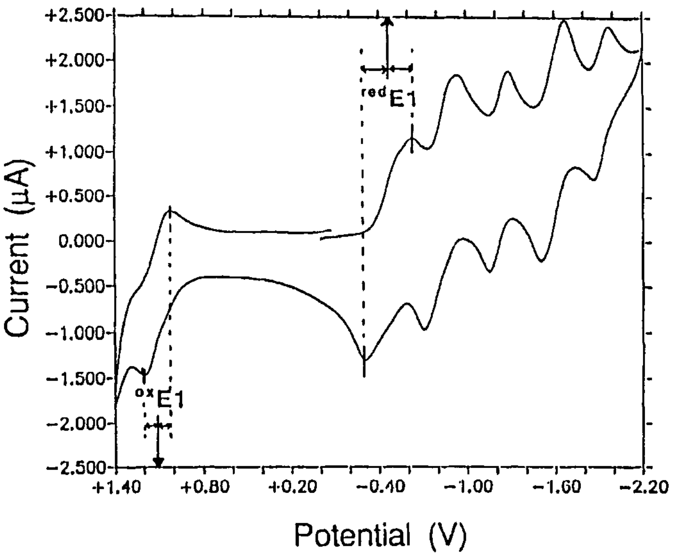

FIGURE 1 The cyclic voltammogram of the C_{2v}' isomer of C_{78} in 1, 2-dichlorobenzene with 0.1M $(n\text{-}Bu)_4NPF_6$. Working and counter electrodes were Pt, the reference electrode Ag/0.01M $AgNO_3$ and 0.1M $(n\text{-}Bu)_4NClO_4$ in CH_3CN.

mass spectroscopy, [5]the purity of the fullerenes was determined to be better than 99 %. It is noted that there exist no isomers for C_{60}, C_{70} and C_{76} but three kinds of isomers for C_{78}.[6] In our experiments, the three isomers of C_{78} are separated into two; one is the C_{2v}' isomer and the other is the mixture of C_{2v} and D_3 isomers. This assignment was revealed from the HPLC spectra, taking into account of the TOF-mass analysis and the optical absorption spectra.[5]

The photocurrent measurements on fullerenes in iso-octane solutions were made by using the VUV light of the synchrotron radiation in the Institute for Molecular Science.[7-8] The photo-ionization energy was obtained from the onset energy of photocurrent spectra.

The cyclic voltammetry was performed by a three-electrode configuration.[9] A typical example of voltammogram is shown in fig.1. The higher fullerene of less than 0.5mg chromatographically purified was dissolved in 5ml of 1,2-dichlorobenzene. The scan started toward the positive potential (scan rate; 20mV/s) at room temperature. All of measurements on fullerenes were made under the same conditions. The data previously reported have been obtained by using the different solvents and electrodes.[10-12] Since the data was quite sensitive to the experimental conditions, the experimental situation presently employed is rather essential for discussion of the nature of fullerenes. The redox potentials are determined by the average values of peak and bottom positions as demonstrated in fig.1.

EXPERIMENTAL RESULTS AND DISCUSSION

The experimental results (V vs. ferrocene/ferrocenium couple) obtained from the CV data are summarized in fig.2 as a function of N. The 1st, 2nd, 3rd and 4th redox potentials for the reduction are presented by solid triangles, squares, rhombus and circles corresponded to $^{red}E1$, $^{red}E2$, $^{red}E3$ and $^{red}E4$, respectively. The open triangles stand for the 1st redox potentials for the oxidation, $^{ox}E1$.

The most striking feature of the cyclic voltammogram is that the multi-step reduction energies up to the 5th were observable. Each step is significantly small less than 0.4 eV and decreases further increasing the size of cage down to 0.25 eV for C_{86}. This indicates that the electron-electron repulsive energy is reduced in a large molecule and many electrons are possible to be doped into fullerenes. In fact, the chemical doping with alkali-metals, such as K_3C_{60}, K_6C_{60},and so on, has been made and the metal- superconductor transition has been discussed by changing a degree of valence of C_{60}.[13] In other words, it is rather easy to change a valence of fullerenes because of the nearly triple-degenerated LUMO state with a small Coulomb repulsive energy.

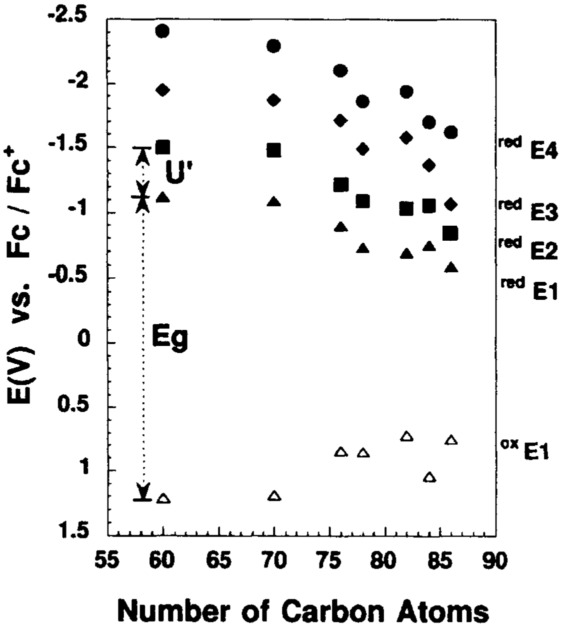

FIGURE 2 Plots of the 1st, 2nd, 3rd, and 4th reduction potentials and the 1st oxidation potential against number of carbon atoms of fullerenes (see text).

The data of the ${}^{ox}E1$ can be directly compared with the ionization energies obtained from the photocurrent measurements, ignoring the solvent effect. In fig.3, the ${}^{ox}E1$ and the ionization energies are plotted by open and solid circles, respectively, as a function of N. The ${}^{ox}E1$ is almost coincident with the ionization energies for all fullerenes by a constant shift of about 5.3 eV.

In fig.4, the difference energies between the ${}^{red}E1$ and ${}^{red}E2$, which corresponds to the Coulomb repulsive energy, U', are plotted against N. It should be noted that the U' of 0.38 eV for C_{60} is considerably smaller than the Coulomb repulsion, U, of about 1 eV obtained by R. W. Lof et al.[14] from the Auger spectroscopy. This difference implies that the Coulomb interaction on C_{60} molecule is effectively reduced by various kinds of relaxation effect, such as solvent effects and electron-molecular vibration interactions, which are absent in the Auger process. Particularly in the case of C_{60}, the relaxation due to the Jahn-Teller interaction plays a crucial role. The Coulomb interaction on the molecule is reduced to about 1/3 of the bare Coulomb interaction.

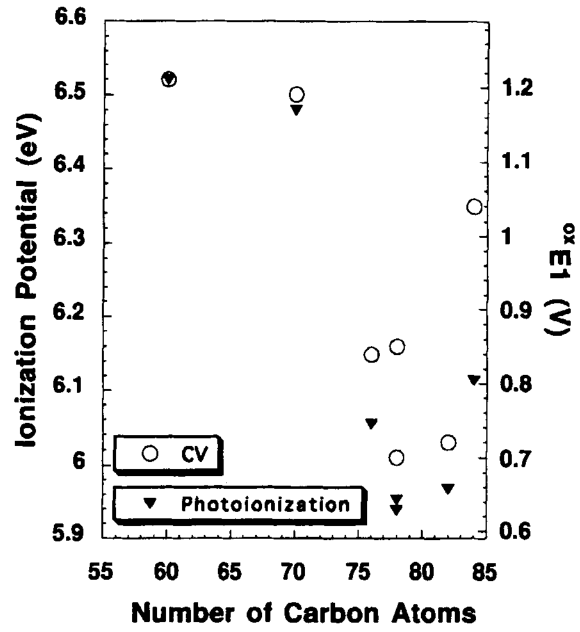

FIGURE 3 Plots of the 1st oxidation energy of fullerenes determined from the CV data presented in fig.2 and the ionization energy (see text).

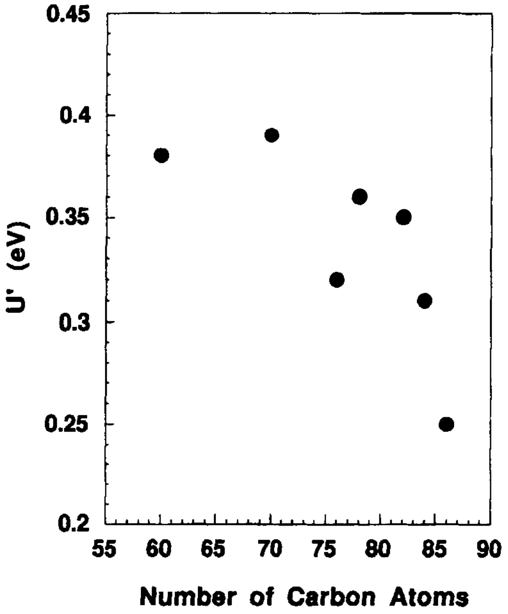

FIGURE 4 Plots of the static electron repulsive potentials, U', against number of carbon atoms of fullerenes.

The other thing to be noted is that the U' decreases with increasing N in a similar manner to the $^{ox}E1$. This result is quite understandable when one considers that the increase of cage size N means a size increase of the electron reservoir. When the case size exceeds 80, the U' is smaller than 0.3 eV, providing a favorable situation for the appearance of metallic states in the doped higher fullerenes.

Fig. 5 shows the absorption spectra in a visible to near-infrared region for saturated toluene solutions of higher fullerene. The spectra are broad with long tails toward the low energy. This weak absorption band can be assigned to the HOMO-LUMO transitions weakly allowed by reduction of molecular symmetry.[5] As N increases, the optical edge defined as an onset of the absorption tails shifts to larger wavelength.

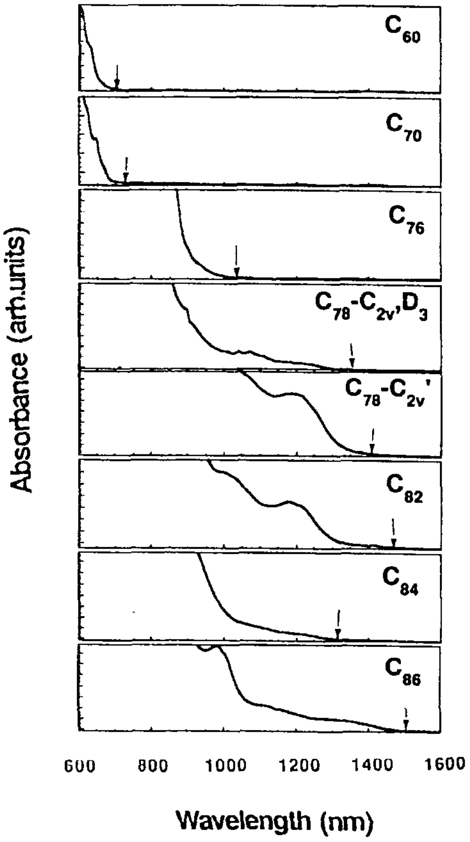

FIGURE 5 The absorption spectra of fullerenes in saturated solution of toluene.

In summary, we plot the absorption edges of fullerenes against 1/N together with those of aromatic hydrocarbons (naphthalene, anthracene, phenanthrene, naphthacene, chrysene, pyrene, perylrene, and coronene) and normal polyenes (ethylene, propylene, butadiene and so on). For the normal polyenes, an extrapolation of the plots reaches ca. 1.4 eV at 1/N = 0. In the case of aromatic hydrocarbons, the gap seems to be extrapolated as a whole to the value of graphite indicated by the arrow. On the other hand, the curve of fullerenes more rapidly decreases with increase of N and supposedly approaches zero at a finite number of carbon atoms. This could not be explained within a framework of normal π-conjugate systems but presumably requires a consideration of the σ-π mixing due to the cage structures or the presence of local deformations around pentagon structures.

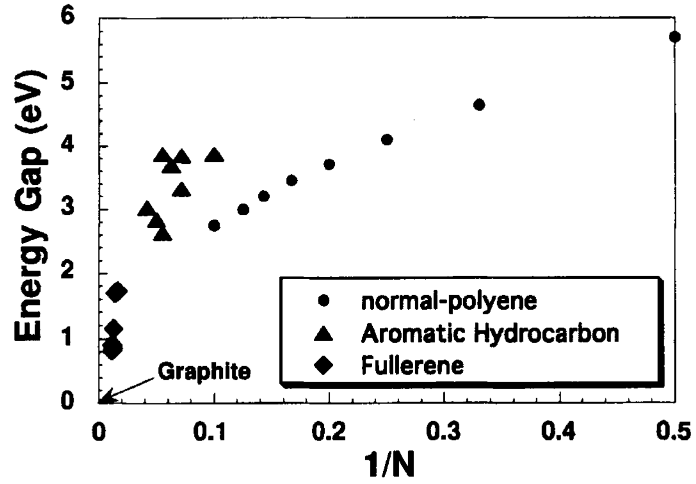

FIGURE 6 Plots of the absorption edges of fullerenes, aromatic hydrocarbons, normal polyenes, and graphite against a reciprocal of a number of carbon atoms. (see text.)

Finally, we point out that the rapid decreasing of the HOMO-LUMO gap in higher fullerenes is worth noting for construction of highly conducting organic materials, particularly C_{78} and C_{86}, having small ionization energies and U'. They are also good candidates for acceptors to form charge-transfer complexes with a low-dimensional metallic conductivity.

DEDICATION

This paper is dedicated to professor Yusei Maruyama on the occasion of his retirements from Institute for Molecular science.

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